

LINEAR, POWER OR EXPONENTIAL: HOW DOES RELATIVE HUMIDITY AFFECT THE RATE OF DEGRADATION OF CELLULOSE?

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Abstract

The way in which relative humidity affects the rate of degradation of cellulose in paper has been studied by several authors, and several equations relating the rate to the relative humidity have been proposed. This paper examines the data critically, and concludes that there is not yet enough evidence to be able to choose unequivocally between linear, exponential or power law relationships. This has implications for the extrapolation of the results of accelerated aging experiments to normal library storage conditions.

1 Introduction

Accelerated aging is a powerful tool for predicting the effect of the environment on the rate of deterioration of collections. The Arrhenius equation is used to extrapolate the rate of deterioration at room temperature from experiments carried out at higher temperatures, where the rate of reaction is great enough to be measurable in a reasonable length of time. The rate of deterioration of paper is affected by the relative humidity (RH) as well as the temperature, and while it is generally agreed that the Arrhenius equation is a good model of the effect of temperature, the way in which RH affects the rate is rather more contentious.

In classical chemical kinetics, the rate of a reaction $A + B \rightarrow \text{Products}$ should depend on the concentration (or more accurately, the activity) of the reactants:

$$\text{Rate} = k[A][B]$$

where k is the rate constant, $[A]$ is the concentration of reactant A and $[B]$ is the concentration of reactant B. If more than one molecule of A or B takes part in the reaction, the rate is then proportional to the concentration raised to the power of the number of molecules concerned: for example, if $A + 2B \rightarrow \text{Products}$ then:

$$\text{Rate} = k[A][B]^2$$

The temperature dependence of k is given by the Arrhenius equation:

$$k = A \exp(-E/RT)$$

where A is the frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

In the degradation of cellulose, the reactants are cellulose molecules, hydrogen ions and water molecules. The concentration of cellulose molecules is large compared to the others and is effectively constant, so it can be ignored. Zou et al.¹ showed that the rate of degradation can be written as:

$$\text{Rate} = k (A_0 + A_2[H_2O] + A_5[H^+][H_2O]) \quad (\text{Equation 1})$$

where $[H_2O]$ is the concentration of water in the paper and $[H^+]$ is the concentration of hydrogen ions. The first term relates to reactions not affected by acidity or moisture content (mostly oxidation), the second relates to hydrolysis (not acid-catalysed) while the third relates to acid-catalysed hydrolysis. The relative importance of these reactions will be different for different kinds of paper.

The concentration of water in paper, or moisture content, is generally taken to be directly proportional to the RH. Strang and Grattan² have argued that the Guggenheim-Anderson-de Boer (GAB) absorption isotherm should be used to represent the dependence of moisture content of paper on RH, but the evidence is not yet good enough to confirm this.

The widely-used Preservation Index (Reilly, Nishimura and Zinn³), developed by the Image Permanence Institute on the basis of an extensive study of the rate of hydrolysis of cellulose triacetate, assumes an exponential relationship between RH and reaction rate (ie rate $\propto \exp(k.RH)$), while the slightly earlier Isoperm model, developed by Donald Sebera⁴, assumes either a linear relationship (rate $\propto RH$) or a power law (rate $\propto RH^n$), where $n > 1$. Michalski⁵ and Pretzel⁶ both favour a power law dependence with $n = 1.3$, but as Michalski points out, there is very little difference between the predictions of the two models at $RH > 20\%$. Large differences only appear at lower RH.

Unfortunately, it is difficult to generalise about the behaviour of paper as different samples show different properties. There is not a great deal of reliable data on the influence of RH on the rate of degradation of paper. Strang and Grattan² used the data of Zou et al.¹ to support their theory, but it will be shown that the dependence of these data on RH can be represented equally well by a power series. Similarly, it will be shown that the data of Kočar et al.⁷ can be equally well represented by a power series or an exponential.

2 Results

In this section the goodness of fit of different functions to the published data will be compared. Fitting involves minimising the sum of the squares of the differences between the observed values of the dependent variable (in this case, k) and the values predicted by the fitting function. Thus if we are fitting the linear function $y = ax + b$ to the data we calculate the sum of the squares of the residuals

$$\sum(y_{obs} - y_{calc})^2 = \sum(y_{obs} - ax - b)^2,$$

otherwise known as χ^2 , and minimise this sum by adjusting the parameters a and b.

Goodness of fit is measured by the correlation coefficient R^2 , defined as:

$$R^2 = 1 - \frac{\sum(y_{obs} - y_{calc})^2}{\sum(y_{obs} - y_{mean})^2}$$

The closer the value of R^2 is to 1 the better the fit.

Traditionally people have preferred to perform a linear fit because it simplifies the calculation, which was an important consideration before the days of easy access to computers. It is also easier to assess by eye how well a straight line fits data. However, we must be aware that if we transform the data in order to obtain a linear fit, for example by taking logarithms of the variables, the best fit to the transformed data is not necessarily the best fit to the original data. In this case, we are interested in being able to predict k, knowing the RH, rather than $\ln k$.

The Solver module in Microsoft Excel uses iteration to find solutions to complex equations, or to find the conditions that will maximise or minimise a function. We can use Solver to adjust the parameters of any

function that we choose to fit the data in order to minimise χ^2 , without needing to transform the data.

Since the actual figures are not given in the published papers, values have been estimated from the graphs. This gives sufficient accuracy for the present purpose, since the data markers on the graphs are large and there are no error bars. The graphs here are plotted in terms of water activity a_H rather than RH ($a_H = RH/100$).

2.1 Zou, Gurnagul, Uesaka and Bouchard (ref. 8)

These authors studied the rate of degradation of Whatman no. 40 filter paper, pH 5.5, at 90° and relative humidities of 0, 40 and 100%.

Their data for the decrease in degree of polymerisation of cellulose can be analysed using the Ekenstam equation⁹:

$$1/DP_t - 1/DP_0 = kt$$

to give values of the rate constant (Fig. 1), and these values are found to lie on a straight line when plotted against the water activity:

$$k = 8.1 \times 10^{-5} a_H + 9.8 \times 10^{-6} \quad R^2 = 0.9997$$

However, with only three data points, this is not totally convincing evidence for a linear relationship.

Time/days	Degree of Polymerisation		
	0% RH	40% RH	100% RH
0	680	680	680
1		630	600
2	640	600	560
4		560	
5	630		475
6.5		535	
7			440
9	600	510	
10			390
12		475	
13	595		
15			340
16		450	
18	580		

Table 1. Rate of degradation of Whatman no. 40 filter paper at 90° and three relative humidities.

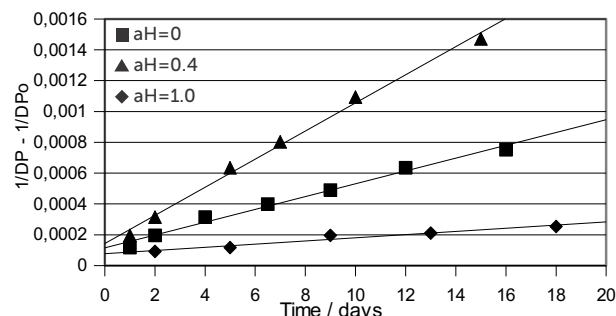


Figure 1: Ekenstam plot of data from ref. 8.

2.2 Zou, Uesaka and Gurnagul (ref. 1)

These authors studied the rate of degradation of bleached bisulfite pulp, pH 4.85, at 90° and five relative humidities.

They draw a sigmoid curve through their data points (Fig. 2), but with only five data points this is not really justifiable – in fact, a linear plot gives a good fit (Fig. 3): $k = 101.8 a_H + 13.426 \quad R^2 = 0.9719$

but a logarithmic plot (ln k vs. a_H) does not, showing that an exponential function is not a good fit to these data. A double logarithmic plot also gives a good linear fit (fig. 4):

$\ln k = 0.6374 \ln(a_H) + 4.7027 \quad R^2 = 0.9901$

but as argued above, we should really consider the best fit to the untransformed data. We first convert the fitting function to its power law form:

$k = 110.244 (a_H)^{0.6374}$

% RH	$k / 10^{-6} \text{day}^{-1}$
2	8.7
17	41
58	71
78	87
100	119

Table 2: Rate of degradation of bleached bisulfite pulp at 90° and various relative humidities.

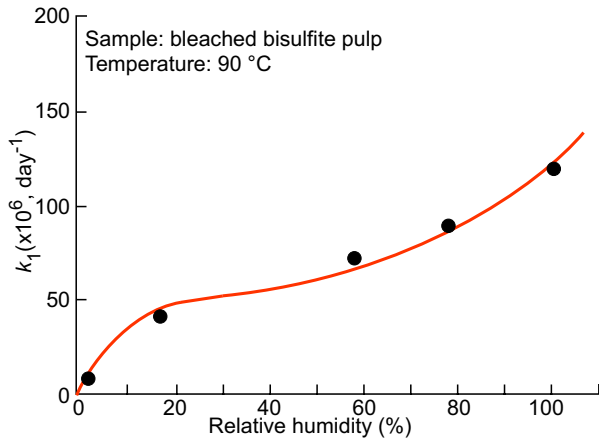


Figure 2: Redrawn from ref. 1. Copyright Springer.

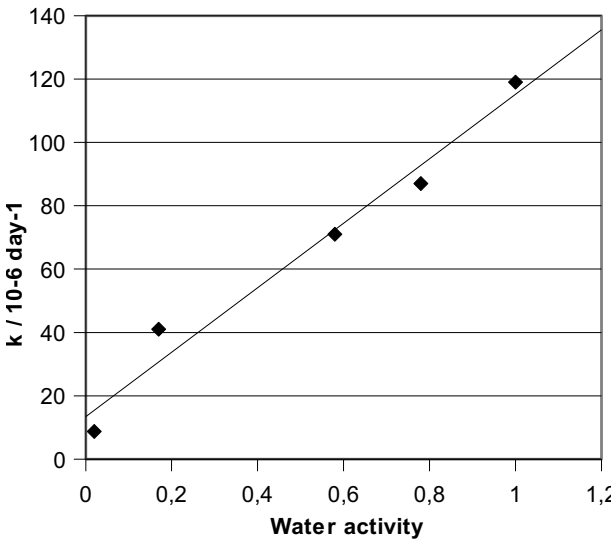


Figure 3: Linear fit of rate constant to water activity.

and then optimise this with Solver to obtain (Fig. 5): $k = 110.8502 (a_H)^{0.6635} \quad R^2 = 0.9721$

Although the value of R^2 is smaller than for the double logarithmic equation, it is comparable to that for the linear equation.

Following Strang and Grattan’s suggestion, the rate of reaction can also be plotted against the moisture content. This gives a good linear fit (Fig. 6): $k = 8.006 MC + 0.8141 \quad R^2 = 0.9911$

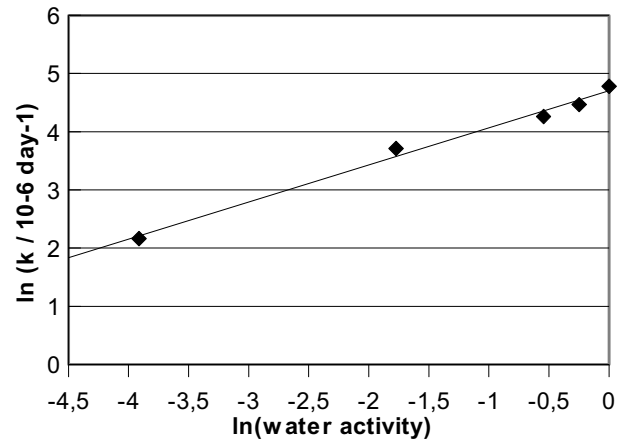


Figure 4: Double logarithmic plot: ln(rate constant) vs. ln(water activity).

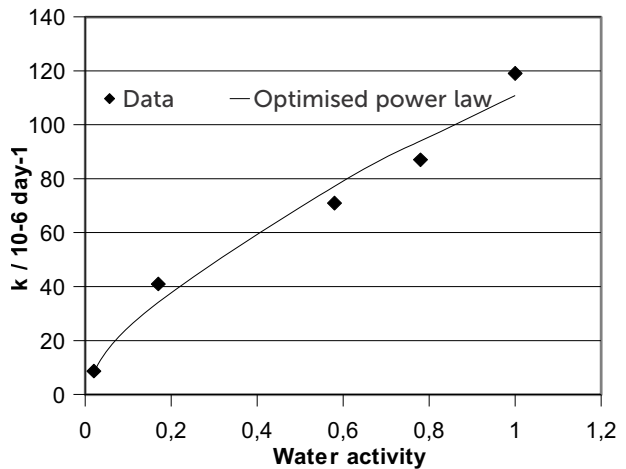


Figure 5: Optimised power law fit of rate constant to water activity.

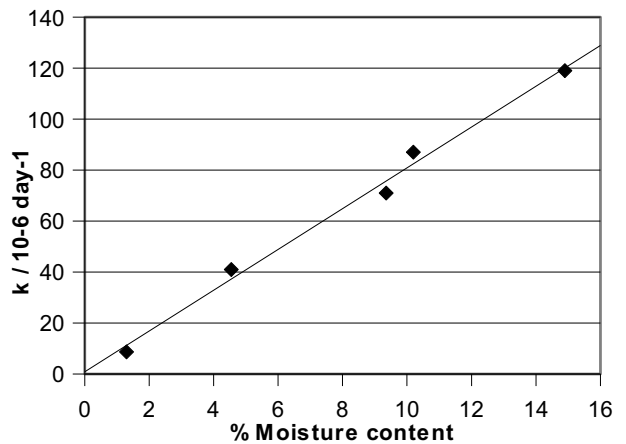


Figure 6: Linear fit of rate constant to moisture content.

These results suggest that there is very little to choose between a linear fit or a power law fit to the k vs RH data and a linear fit to the k vs moisture content data. Certainly the difference is insufficient to give unequivocal support to one equation.

2.3 Kočar, Strlič, Kolar, Rychly, Matisova-Rychla and Pihlar (ref. 7)

These authors studied the rate of degradation of three different papers (Whatman no. 1 (Wh), bleached sulphate softwood pulp (SA) and cotton pulp (C)) at 90° and various relative humidities (Fig. 7).

The rates of degradation of the softwood pulp and the cotton pulp were more or less unaffected by RH, but the rate of degradation of the Whatman no. 1 filter paper increased markedly. This is because the Whatman paper is slightly acidic (pH of extract = 6.6) while the sulphate pulp and cotton pulp are slightly alkaline (pH 7.2 and 9.6). By inspection of the graphs, it appears from these data that for all three papers the rate of the reaction that is unaffected by acidity or RH (A_0 in Equation 1) is significant and in the region of $0.3 \times 10^{-10} \text{ s}^{-1}$. We therefore need to include a constant term in our optimised fitting function for the Whatman paper: $k = a \cdot \exp(b \cdot a_H) + c$.

Since we cannot calculate the pre-exponential factor (a), the coefficient of a_H (b) and the constant term (c) in one operation, we first perform a linear fit of $\ln k$ to a_H and obtain:

$$\ln k = 2.4963 a_H - 0.9744 R^2 = 0.9735$$

which in exponential form gives:

$$k = 0.3774 \exp(2.4963 a_H)$$

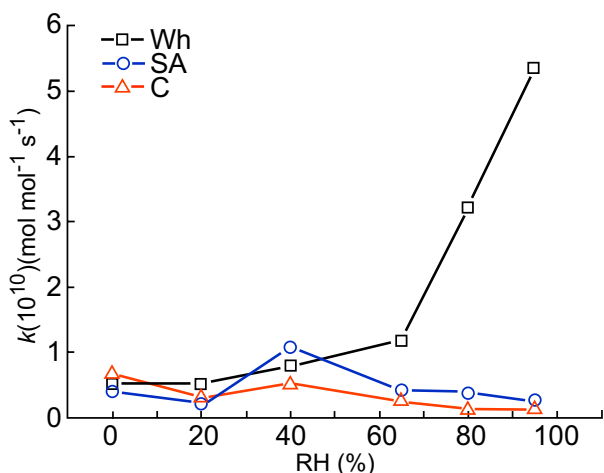


Figure 7: Redrawn from ref. 7. Copyright Elsevier.

	Whatman	Sulphate pulp	Cotton pulp
% RH			
0	0.54	0.43	0.68
20	0.54	0.25	0.32
40	0.82	1.11	0.50
65	1.21	0.43	0.25
80	3.29	0.39	0.14
95	5.43	0.25	0.14

Table 4: Rate of degradation of Whatman no. 1 (Wh), bleached sulphate softwood pulp (SA) and cotton pulp (C) at 90° and various relative humidities.

We can now use this as the starting point for optimising the fitting function. We set Solver to minimise the value of χ^2 , subject to the condition that $0 < c < 0.54$ (to avoid negative values of the rate). This gives the best fit as (Fig. 8):

$$k = 0.0570 \exp(4.7356 a_H) + 0.3949 \quad R^2 = 0.9828$$

Similarly, we can perform a linear fit of $\ln k$ to $\ln a_H$:

$$\ln k = 1.3914 \ln(a_H) + 1.3509 \quad R^2 = 0.8233$$

which as a power law gives:

$$k = 4.0205 (a_H)^{1.3914}$$

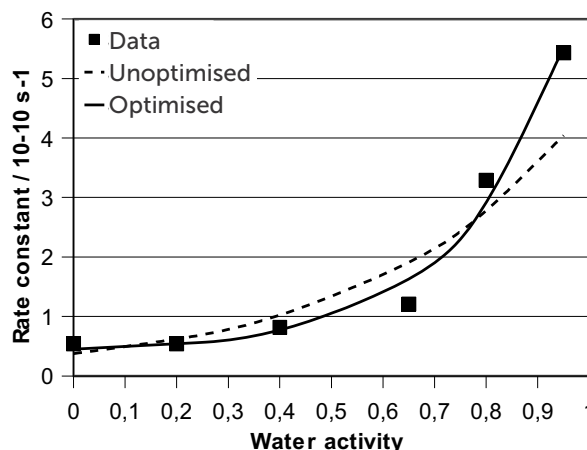


Fig. 8: Unoptimised and optimised exponential fit to data from ref. 7.

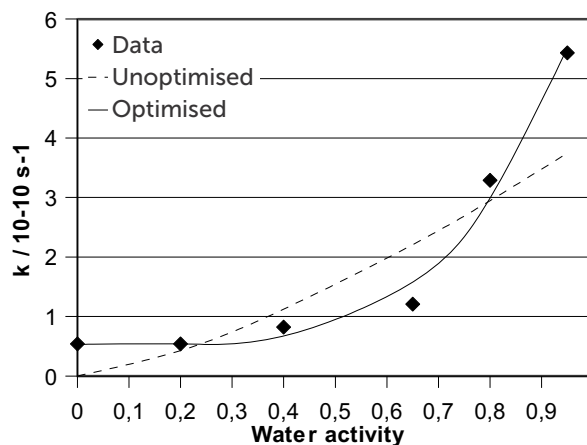


Fig. 9: Unoptimised and optimised power law fit to data from ref. 7.

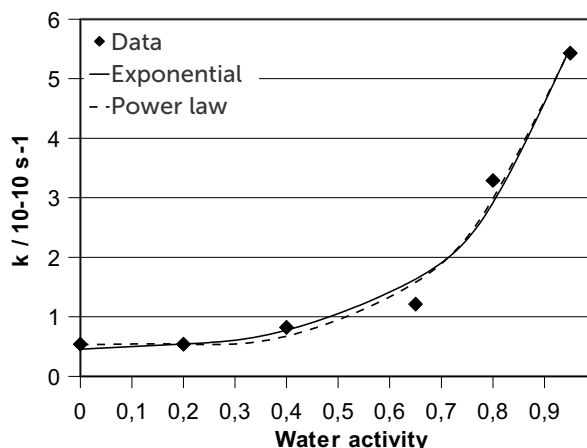


Fig. 10: Optimised exponential and power law fits to data from ref. 7.

and which can be optimised in the same way to give (Fig. 9):

$$k = 6.1431 (a_H)^{4.1064} + 0.537 \quad R^2 = 0.9871$$

This result could be interpreted to mean that four hydrogen ions are involved in the hydrolysis of the cellulose molecule, but this is fairly improbable, so it is best viewed as just a mathematical artefact. There is very little to choose between the optimised exponential and the optimised power law fits to the original data, as can be seen in fig. 10.

3 Conclusions

Curve fitting of data is generally done either to provide experimental backing to a theoretical equation, or to find an empirical equation that gives the best fit to the data for predictive purposes. In some cases there are good theoretical reasons to expect the data to fit a particular equation, and if the data are accurate there will be a great deal of confidence in the result. In other cases there may be competing theories, in which case accurate data are vital to help decide which theory is more likely to be true, or there may be no theory, in which case an empirical description of the data may be all that can be hoped for. In such cases, the simplest equation that fits the data, with the smallest number of fitting parameters, should be preferred.

Linear regression is very commonly used to assess how well experimental data fit a theoretical equation, even if the data have to be transformed in order to give a straight line. However, the parameters that give the best fit to a straight line do not necessarily give the best fit to the untransformed data. Simple methods now exist whereby data can be fitted to an arbitrary function using widely available software. The parameters found in this way give a better fit to the data.

This paper shows that the experimental data on the effect of relative humidity on the rate of degradation of various kinds of paper can be represented equally well in one case by a linear equation or a power law, and in another by an exponential or a power law. This is not a criticism of the work of the original authors: these experiments are time consuming and require a large number of replicates to get reliable results. In order to be able to establish conclusively whether a linear, exponential or power law is most appropriate, more experiments would need to be done, particularly at lower relative humidities – where the rate of reaction is slower and the experiments would take longer to complete. It is also clear that different papers behave in different ways: as remarked above, the rates of degradation of two of the papers studied by Kočar et al. were unaffected by relative humidity and it may well be that there is no single equation that is valid for all kinds of paper.

4 References

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